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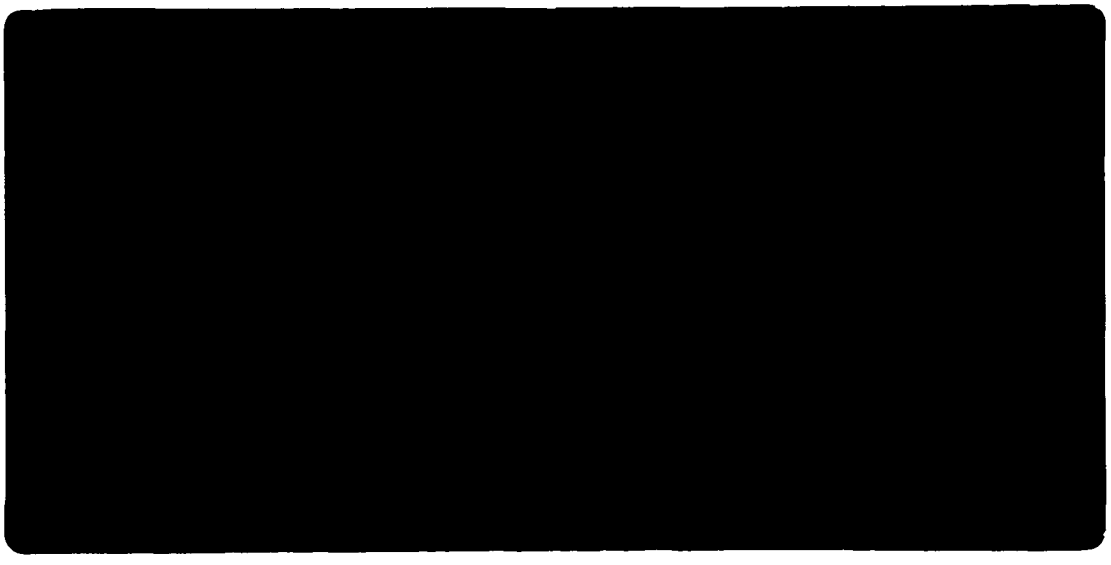

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KEYWORDS

E1 concentrates, closed cycle, chlorine, black liquor, combustion, HCl emissions, swelling, ultrafiltration

ABSTRACT

Laboratory data indicate that the combustion heating values, combustion rates, and HCl emissions for black liquor combustion are not noticeably affected by addition of controlled amounts of E1 concentrate liquor (from ultrafiltration). Combustion tests using the IPST single droplet furnace show clearly that the rate of burning of 100% E1 concentrate liquor is dramatically slower (by about a factor of five) than the burning rate of black liquor. This is explained by the liquor swelling behavior; the E1 concentrate liquor swells much less than black liquor. However, for mixtures of E1 concentrate liquor with black liquor, the combustion rate of the liquor mixture is the same as for pure black liquor when the level of E1 concentrate addition is below 25% (wt/wt basis). Measured HCl emissions from burning liquor mixtures showed that HCl emissions were unaffected by addition of E1 concentrate at levels of addition below 10%. Beyond 10% addition levels, HCL emissions increased to a maximum at 100% E1 concentrate liquor. The levels of E1 concentrate addition expected at a typical mill are close to 1%.

INTRODUCTION

There is increasing interest in moving toward closed cycle technologies such as ultrafiltration, polymer treatment, and others at existing bleached kraft mills. These closed cycle technologies could potentially decrease water usage rates and pollutant discharge rates from bleach plants. However, implementation of these technologies for the purpose of concentrating bleach plant effluents will produce undesirable concentrated side streams containing high concentrations of lignin, inorganic chlorides, and chlorinated organics. Presently, there is a lack of generally accepted disposal methods for handling such chlorine containing-concentrated streams. This problem was identified in a recent technical bulletin[1] of the National Council of the Paper Industry for Air and Stream Improvement (NCASI) as one of the major technical difficulties associated with closed cycle technologies at bleached kraft mills.

The only demonstrated technology for treating these concentrated streams is additional concentration in multiple-effect evaporators followed by burning in recovery furnaces.[2] Potentially negative impacts of burning these streams in the recovery furnace are the effects of increased levels of chloride and chlorinated organics on the combustion process and its associated emissions. The seriousness of these impacts is not well understood. In particular, data are not available on how the addition to black liquor of concentrates high in chlorine will affect flue gas emissions (such as HCl and chlorinated organic compounds).

Data have been reported[3,4] on the chemical compositions, heating values, and combustion rates of chlorine-containing concentrates. The concentrates were found to be very similar to typical kraft black liquor in carbon contents and heating values. Burning rates for the concentrate solids were found to be similar to typical burning rates for black liquor solids. Two limitations of the applicability of the data obtained in this work are: (1) the concentrate solids were not compared to black liquor solids obtained from the same pulping operation; and (2) the concentrate burning rates were determined for finely ground (50-100 μm particle size) moisture-free solids. To evaluate the feasibility of burning chlorine-containing concentrates in recovery furnaces, it is of interest to know how these concentrates will burn as liquors.

The purpose of this work is to more clearly determine the impacts on recovery furnace operation which would be brought about by adding controlled amounts of chlorine-containing liquor (i.e., concentrated bleach plant effluent) to black liquor from the same pulping operation. The impacts on liquor composition, liquor heating value, burning rate, and HCl emission during burning are examined; the subject of corrosion is not addressed in this work.

EXPERIMENTAL

For this study, E1 effluent from the first extraction stage and concentrated black liquor were obtained from a bleached (approximately 30% ClO_2 substitution) kraft mill pulping softwood. Chlorine-containing concentrate was produced by ultrafiltration of the E1 effluent and further concentration of the ultrafiltration concentrate in a rotary evaporator under N_2 at 70-85°C (partial vacuum).

Combustion of the liquors was performed using the IPST single droplet furnace, which has been described in detail elsewhere.[5] Controlled amounts of E1 concentrate liquor were mixed with black liquor. Small droplets (about 2.5 mm diameter) of the mixed liquor at 65% liquor solids were formed on nichrome wire hooks and inserted into the reaction chamber of the furnace. A gas mixture (5% O_2 in 95% N_2) preheated to furnace temperature (800°C) was drawn continuously through the reaction chamber such that the stationary droplets were exposed to a convective environment of 0.6 m/s gas velocity.

Observation of droplets as they underwent drying, devolatilization and swelling, and char burning were made with a video camera by recording the image through a quartz window in the reaction chamber wall. Determinations of burning rates were made by subsequent careful examination of the video recordings.

Measurements of HCl emissions were made using the tube furnace shown in Figure 1. A known quantity (100-200 mg) of mixed liquor was placed in a

ceramic boat and inserted through the furnace door into the end of the combustion tube. Air was drawn at a controlled rate through the tube. Tube length and gas flow rate were sufficient to provide for complete combustion of the boat contents.

The products of combustion were drawn out of the furnace, cooled, filtered, and bubbled through an aqueous solution to capture gaseous HCl as dissolved chloride. The chloride concentration of the solution was determined by using HPLC (high pressure liquid chromatography). Measurements were also made of chloride in the rinsate used to clean the combustion tube, chloride on the fume filter, and chloride in the ash residue remaining in the boat after combustion. Material balances on chlorine comparing the sum of chloride in the postcombustion measurements to the chlorine initially in the mixed liquor showed that all of the chlorine was accounted for.

RESULTS AND DISCUSSION

Elemental Compositions

Elemental compositions and heating values are shown in Table I for both the E1 concentrate liquor and the black liquor. Carbon contents and heating values were similar. The E1 concentrate higher heating value (HHV) is somewhat lower, but the E1 concentrate has much less sulfur. When the energy required to convert the sulfur from sulfate to sulfide is accounted for, the E1 concentrate has a slightly greater net heating value (NHV). This is consistent with the earlier reported observation[3] that E1 ultrafiltration concentrates have heating values at least as great as black liquors when compared on the same basis of moisture level. This indicates that mixing of E1 concentrate liquor with black liquor will not result in derating the liquor heating value.

As noted in Table I, the E1 concentrate liquor has about 20 times more chlorine than black liquor. Approximate material balances were made and showed that if all the E1 effluent in a typical bleached-kraft mill were ultrafiltered, and all of the concentrate mixed with weak black liquor, the resulting liquor solids would consist of about 99% black liquor solids and 1%

E1 bleach plant solids. This would give a hybrid fuel with a chlorine content of 0.56 wt/wt% instead of the 0.46% as shown in Table I for pure black liquor. This would be an increase of 21% in the fuel chlorine level. This level of chlorine would exist in the liquor on the first pass; with recycle in the chemical recovery cycle, the black liquor chlorine concentration could build to greater than 0.56 wt/wt%. The steady-state level would depend on the various rates of chlorine purge from the recovery cycle.

Combustion Characteristics

Results from burning mixtures of E1 concentrate liquor with black liquor in the single droplet furnace are shown in Figures 2-4. Each data point is the average of five burns at that condition. Drying time was determined from the time of insertion of the droplet into the furnace to the time of initial existence of a visible flame around the droplet. Devolatilization time was determined from the time of initial flame to the time of flame extinction. Char burning time was determined from the time of flame extinction to the time when the melted inorganics coalesced into a smelt bead.

As seen in Figures 2 and 3, addition of E1 concentrate liquor at levels up to 50% concentrate had no noticeable effect on drying and pyrolysis times. Determination of drying and devolatilization times at addition levels greater than 50% concentrate addition was made difficult by the fact that the concentrate liquor did not burn in distinctly identifiable stages like black liquor.

Char burning times are shown in Figure 4. Addition of up to 25% E1 concentrate liquor to black liquor did not noticeably affect char burning times. Addition beyond the 25% level resulted in a rather abrupt five-fold increase in char burning times.

At least a partial explanation for the dramatic increase in char burning time is the swelling behavior. Black liquor droplets swell slightly during drying and undergo tremendous swelling during devolatilization. It has been shown that liquors which swell less burn slower.[6] The maximum swollen volumes for the test burns with E1 concentrate liquor added to black liquor are shown

in Figure 5. At less than 25% addition, swelling actually increased somewhat. But at addition levels greater than 25%, swelling decreased by a factor of 10. With this much decrease in swelling, the char burn time is expected to increase, as demonstrated in Figure 4.

The implications of this data for recovery furnace burning are important. Burning of mixtures at or near 1% addition of E1 concentrate liquor (approximately the expected steady-state addition level) should not affect swelling or burning time. However, addition at higher levels (> 20%) could have tremendous impacts on swelling and greatly decrease the burning rate.

HCl Emissions

The measured HCl emissions from combustion in the tube furnace (see Figure 1) are shown in Figure 6. The levels of HCl emissions for 100% black liquor were approximately 0.4 g HCl per kg of black liquor solids, which means that about one-tenth of the black liquor chlorine was converted to HCl. Most of the black liquor chlorine was found in the fume and ash (smelt) products.

This HCl level (0.4 g HCl/kg solids) is equivalent to about 60 ppm HCl in the combustion product gas, if reported on a basis of 8% O_2 concentration in the gas. The precise level of HCl emission should not be considered to represent the HCl emission level of a recovery furnace burning this black liquor. Because the time, temperature, and mixing histories of gases and particles in the laboratory furnace were not the same as those in a recovery furnace, there is no reason to believe that the emission levels from the two should be the same. What is important for the laboratory furnace HCL emission levels is the result when E1 concentrate liquor is added to the black liquor.

For levels of E1 concentrate liquor addition less than 10%, the HCl emission rate was not significantly affected. This was true even though the chlorine present in a mixture of 10% E1 concentrate liquor with 90% black liquor was 1.45% (over three times the 0.46% level in pure black liquor). The fact that there was no increase in this range is presumed due to the dominant effect of the inorganics present (primarily sodium). As mentioned above, only a small

fraction (one-tenth) of black liquor chlorine was converted to HCl. The sodium compounds in fume and smelt were dominant in controlling the fate of the chlorine. It seems reasonable that even though the chlorine content was tripled, it was still relatively small when compared to sodium content, and a net change in HCl was seen only when more chlorine than this was added.

At levels of E1 concentrate liquor addition beyond 10% (see Figure 6), HCl emission levels increased, showing a maximum of 470 ppm for 100% E1 concentrate liquor. This represents about 5% of the total chlorine in E1 concentrate liquor which was converted to HCl. Thus, only half as much of the total chlorine was converted to HCl for E1 concentrate liquor, as for black liquor. This is consistent with the earlier reported chlorine trapping data,[4] which showed that during pyrolysis of bleach plant solids containing a molar excess of sodium, most of the organic chlorine was trapped as NaCl rather than emitted as HCl.

A limited number of HCl measurements were also made during combustion of liquor mixtures in the IPST char bed reactor. This facility consists of a drop tube furnace in which liquor droplets fall downward through upflowing hot gases, dry, partially pyrolyze, and collect and burn on a char bed. Levels of HCl emission (not shown in Figure 6) were not seen to change significantly for E1 concentrate liquor addition levels of 0, 0.5, and 1.0%.

CONCLUSIONS AND RECOMMENDATIONS

The implications of these data for recovery furnace burning are important. Burning of mixtures at or near 1% (approximately the expected steady-state addition level) should not affect fuel heating value, swelling, or burning time. However, addition at higher levels could have tremendous impacts on swelling and greatly decrease the burning rate. The combustion rate decreased dramatically, and HCl emissions increased for higher addition levels.

The direction of future work in this area of combustion of bleach plant solids should be aimed at the study of concentrates from more modern effluents,

such as from 100% ClO_2 substitution bleaching or from totally chlorine-free bleaching.

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TABLE I.
ELEMENTAL COMPOSITIONS OF BLACK LIQUOR AND E1 CONCENTRATE LIQUOR, wt/wt% of solids

	Black Liquor	E1 Concentrate Liquor
C	36.9	39.2
H	4.71	3.29
O	32.5	32.4
S	4.90	0.51
Na	18.5	14.2
Cl (Org)	–	5.95
Cl (Inorg)	0.46	4.43
HHV	6,320	5,720 (BTU/lb)
NHV	5,250	5,340

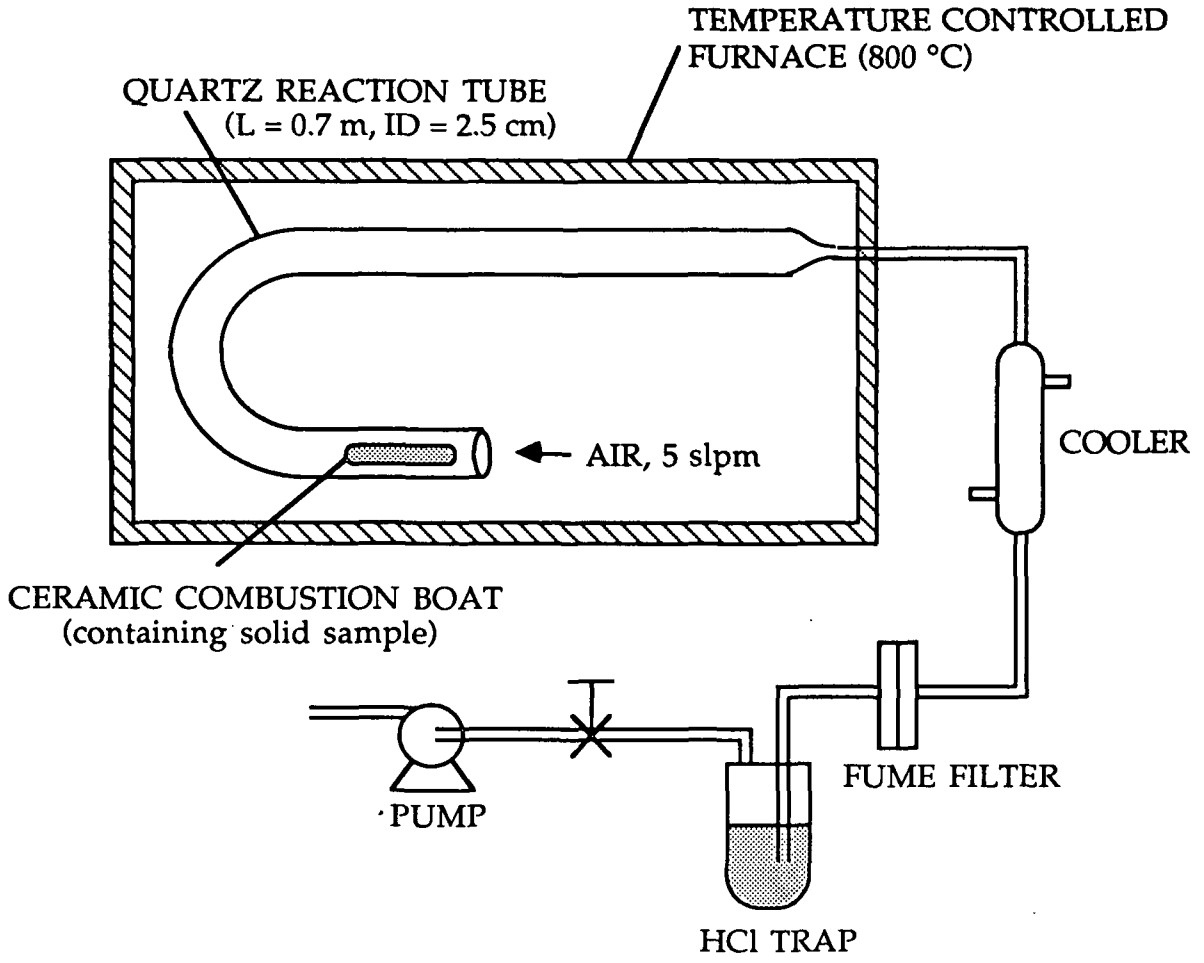

Figure 1. Laboratory scale furnace used for HCl emission measurements.

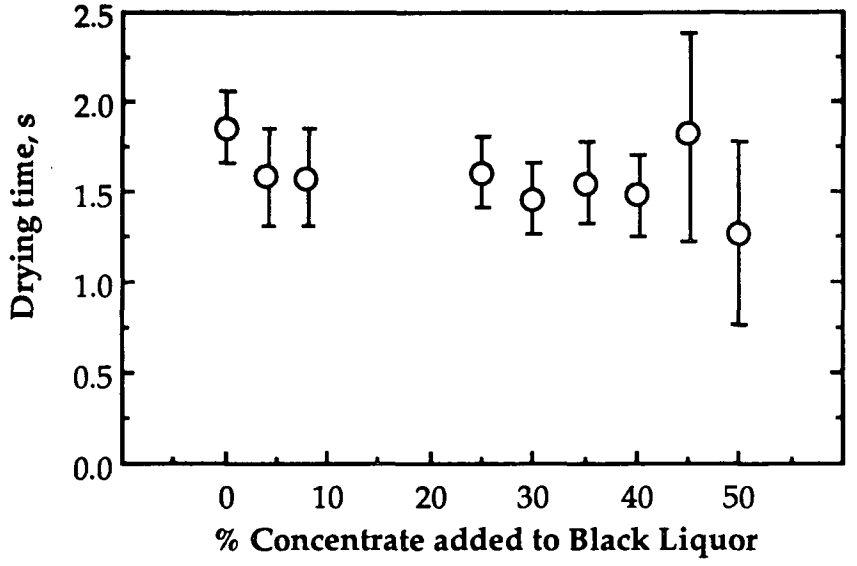

Figure 2. Drying times for mixtures of E1 concentrate and black liquor as determined from video recordings of single droplet burns: 800°C furnace temperature, 5% O_2 in 95% N_2 furnace gas, 0.6 m/s gas velocity, 65% solids liquor, 2.4 mm liquor droplets. Error bars represent two standard deviations.

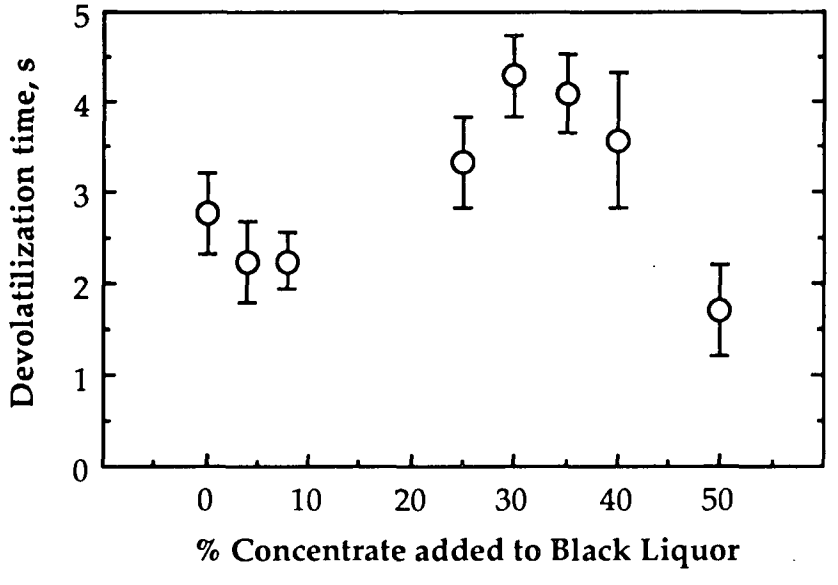

Figure 3. Devolatilization times for mixtures of E1 concentrate and black liquor as determined from video recordings of single droplet burns: furnace conditions same as in Figure 1.

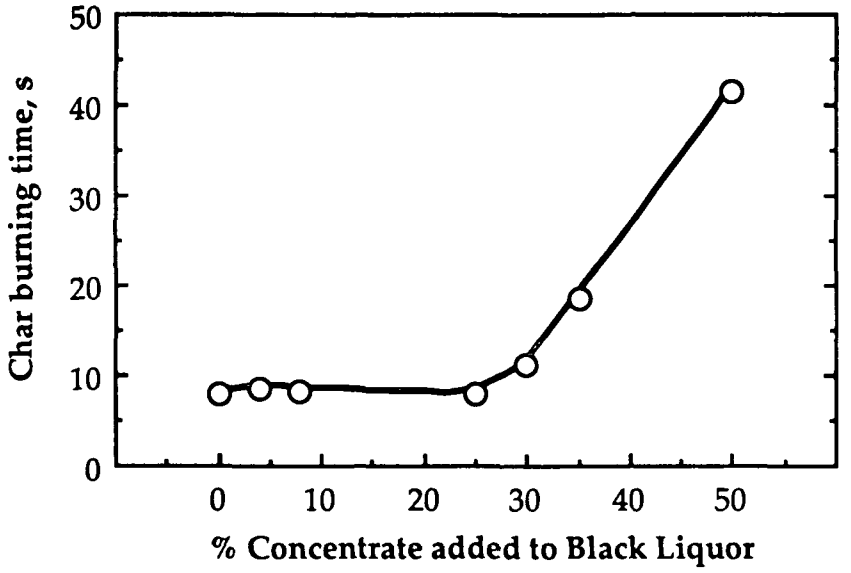

Figure 4. Char burning times for mixtures of E1 concentrate and black liquor as determined from video recordings of single droplet burns: furnace conditions same as in Figure 1.

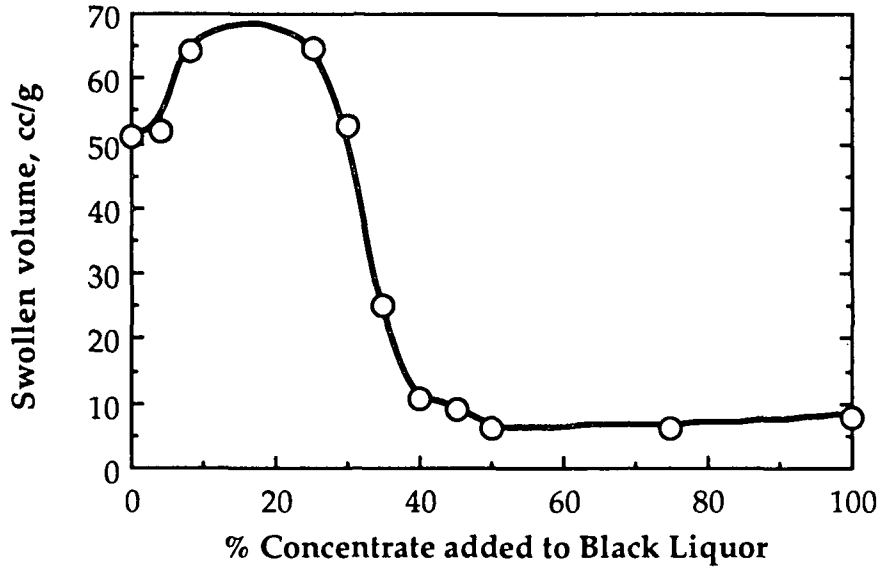

Figure 5. Maximum swollen volumes for mixtures of E1 concentrate and black liquor as determined from video recordings of single droplet burns: furnace conditions same as in Figure 1.

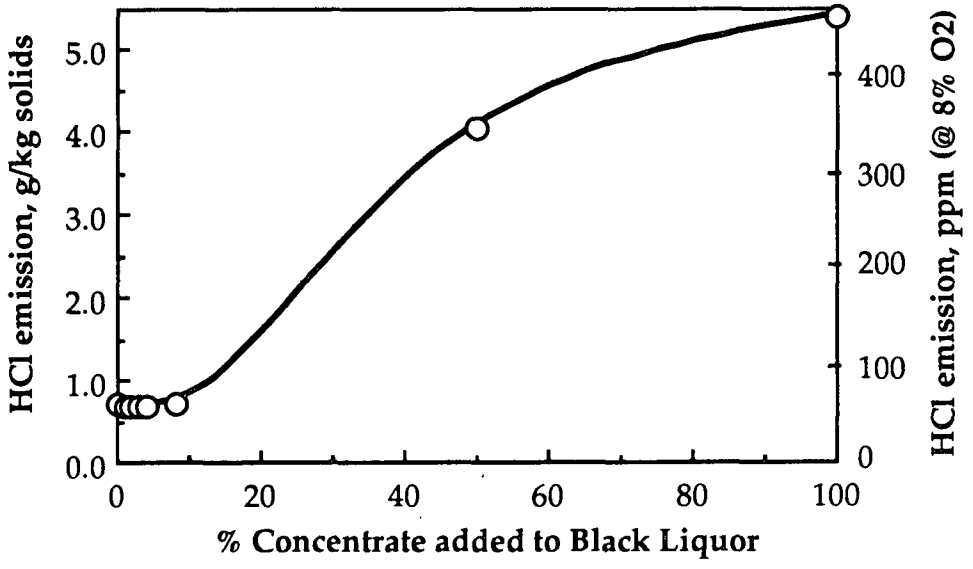

Figure 6. Effect of E1 concentrate addition on HCl emissions from laboratory scale black liquor combustion.